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(54) Title: POLYIMIDE COMPOSITE POWDER, AND METHOD FOR PRODUCING THE SAME. (57) Abstract The polyimide composite powders of the present invention are characterized by being composed of an organically converted fine clay mineral obtained by the organic conversion of fine clay mineral, and a polyimide that covers this organically converted fine clay mineral.		

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TITLE**POLYIMIDE COMPOSITE POWDER, AND METHOD
FOR PRODUCING THE SAME****BACKGROUND OF THE INVENTION**

5 The present invention relates to polyimide composite powders, and methods for their production. More specifically, it relates to powders obtained by dispersing an organically converted clay mineral in a polyimide resin, starting-material powders for obtaining polyimide composite molded articles having excellent dimensional stability, and methods for their production.

10 **BRIEF DESCRIPTION OF THE RELATED ARTS**

Because polyimides have excellent thermal properties, mechanical properties, electrical resistance, resistance to chemicals and the like, they are suitable for use in films, flexible printed circuit boards, insulators in electric motors, and electrical wire coating materials. However, there are a number of
15 problems with the practical use of these materials, such as their large gas permeability and their large heat expansion coefficient.

With regard to polyimide molded products, Japanese unexamined patent publication Kokai No. 1-292,035 (1989) discloses a method in which a polyamic acid serving as the intermediate polymer for the polyimide is synthesized in a
20 basic solvent (pyridine or β -picoline), then is brought into contact with a poor solvent (acetone) of polyamic acid and is precipitated, thereby forming a finely divided, non-crystalline polyamic acid powder, following which the powder thus obtained is rendered into a polyimide powder by means of a hot ring-closing reaction, and this polyimide powder is molded by compression and sintering so
25 as to give plastic molded articles. This patent application also discloses that the use of a carbonaceous substance such as graphite as a filler in the polyimide powder enhances the wear resistance, but no mention is made of any attempt to enhance the resin properties by adding other inorganic fillers.

As for polyimide composites, according to Kokai No. 4-33,955 (1992), a polyamic acid serving as the intermediate polymer for polyimide is uniformly mixed with clay that has been organically converted with organic onium ions in an aprotic polar solvent (e.g., N,N-dimethylacetamide and N-methylpyrrolidone), then the liquid mixture is cast so as to obtain a polyamic acid film. A hot ring-closing reaction is subsequently carried out on the polyamic acid film thus obtained, thereby giving a polyimide film in which the organically converted clay mineral has been uniformly dispersed.

When organically converted clay is mixed into a solution of polyamic acid in a basic solvent, as in the method for producing polyimide molded articles in above-mentioned Kokai No. 1-202,035, agglomeration of the organically converted clay arises, as a result of which the organically converted clay does not uniformly disperse within the polyimide matrix. Hence, the desired polyimide composite having a high dimensional stability cannot be obtained in this way. The reason is that, although the organically converted clay uniformly disperses in aprotic polar solvents, it does not uniformly disperse within basic solvents.

Moreover, in precipitation and deposition methods in which a liquid mixture of polyamic acid and organically converted clay is prepared with an aprotic polar solvent that uniformly disperses the organically converted clay, because the aprotic polar solvent has a high polyamic acid solubility compared with basic solvents, it has been impossible to obtain finely divided powders suitable for molding polyimide.

In light of the above-described circumstances, the object of the present invention is to provide both composite powders in which an organically converted clay mineral has been uniformly dispersed in polyimide molded articles and which has an excellent dimensional stability, as well as methods for the production of the same.

SUMMARY OF THE INVENTION

The polyimide composite powder of the present invention is composed of an organically converted fine clay mineral and a polyimide that disperses and retains this clay mineral. This composite powder can be produced by a mixing
5 step in which an intermediate polymer of the polyimide and an organically converted fine clay mineral are dissolved and dispersed within an aprotic polar solvent so as to give a slurry-like liquid mixture, and a powder conversion step in which this slurry-like liquid mixture is spray-dried, thereby forming a finely divided powder-like polyimide-clay hybrid in which the organically converted
10 fine clay mineral is dispersed within the polyimide resin.

Because the organically converted fine clay mineral is uniformly dispersed within the polyimide, this becomes a starting material powder from which molded articles having a small thermal expansion coefficient can be easily obtained.

DETAILED DESCRIPTION OF THE INVENTION

Aprotic polar solvents uniformly disperse organically converted clay and dissolve polyamic acid. In addition, when an aprotic polar solvent slurry in which this organically converted clay has been dispersed and polyamic acid has been dissolved is sprayed and dried without modification, a finely divided
20 powder in which the organically converted clay and the polyamic acid are uniformly dispersed can be formed.

The polyimide composite powders of the present invention are characterized by being composed of an organically converted fine clay mineral obtained by the organic conversion of fine clay mineral, and a polyimide that
25 covers this organically converted fine clay mineral.

The method for producing polyimide composite powders of the present invention comprises a mixing step in which a polyimide intermediate polymer and an organically converted fine clay mineral obtained by the organic conversion of a fine clay mineral are dissolved and dispersed in an aprotic polar

solvent so as to give a slurry-like liquid mixture; and a powder conversion step in which said slurry-like liquid mixture is spray-dried, thereby forming a polyimide-clay mineral composite in the form of a finely divided powder in which said organically converted fine clay mineral is dispersed within the
5 polyimide resin.

Here, "organically converted clay mineral" refers to a clay mineral to which organic onium ions have been bonded by treatment with a compound containing organic onium ions.

"Organic onium ion" refers to an organic compound having an onium
10 ion at one end of the main chain. Examples that may be cited of onium ions include ammonium ions, pyridinium ion, sulfonium ion and phosphonium ion. The main chain is composed of a straight-chain or branched carbon chain, and cyclic structures may be included in part of the main chain. The other end of the main chain does not necessarily have to be a hydrogen, it being possible for this
15 to be a hydroxyl group, an amino group, a carboxyl group, a nitro group, a sulfone group or derivatives of these. In order to expand the interlayer spacing of the clay mineral and fully assure its dispersion effects, it is preferable that the number of carbons in the main chain be at least 6. In order to preserve the affinity with the aprotic polar solvent, it is desirable that the number of carbons
20 in the main chain be no more than 20. When consideration is given to all of the above points, the most preferable organic onium ions are alkylammonium ions such as a laurylamine ion, myristylamine ion, palmitylamine ion or stearylamine ion.

The organic conversion of the clay mineral by means of an organic
25 onium ion (i.e., formation of the organically converted clay) is carried out by the substitution of organic onium ions for exchangeable inorganic ions on the clay mineral. There is no particular restriction on the weight ratio of the organic onium ions and the clay mineral, although it is preferable that the above-

mentioned exchangeable inorganic ions be adequately substituted with the organic onium ions.

There is no particular restriction on the synthesis of the organic onium ion-containing clay mineral, it being possible to carry out synthesis by various methods. Synthesis can be carried out, for example, by mixing the clay mineral and the organic onium ions within one or more solvents selected from among water, methanol, ethanol, propanol, ethylene glycol, 1,4-butanediol, glycerol and the like. For example, when the clay mineral is montmorillonite, the use of one or more solvents selected from among water, methanol and ethanol is preferable.

The clay mineral used in the present invention is preferably a lamellar clay mineral. Examples that may be cited of this lamellar clay mineral include smectite-type clay minerals such as montmorillonite, saponite, beidellite and stevensite, as well as vermiculite, halloysite and swellable mica. It is preferable for the cation-exchange capacity of lamellar clay minerals to be about 50-300 meq/100 g, and for this to have a large contact surface area with the polyimide to be reacted or the starting monomer thereof. When the cation-exchange capacity exceeds 300 meq/100 g, the interlayer bonding force of the lamellar clay mineral becomes too large, thereby making it difficult to widen the interlayer interval and resulting in poor dispersibility within the polyimide. On the other hand, when the cation-exchange capacity falls below 50 meq/100 g, this results in an inadequate amount of adsorbed organic onium ions, thereby making affinity with the polyimide inadequate.

The particle size of the clay mineral is 0.1-100 μm , and preferably 1-20 μm . Moreover, it is preferable that this clay mineral be of a flake-like type having the above-indicated particle size. Powders in which the particle size exceeds 100 μm have a small surface area, making it impossible to obtain good molded articles when compression/sinter molding is carried out. On the other hand, when the particle size is less than 0.1 μm , the powder is too fine, as a result of which the workability during molding decreases. More specifically, the

fine clay mineral is preferably a lamellar clay mineral having no more than five layers, and is ideally a single-layer clay mineral composed of lamellar clay mineral that has been delaminated into single layers. The lamellar clay mineral in which the number of layers is five or less should represent at least 50%, and preferably at least 70%, of the overall clay mineral (where the total amount of clay mineral is 100%).

The polyimide intermediate polymer used in the present invention can be obtained by a polycondensation reaction between a diamine and an acid dianhydride, and may be, for example, a polyamic acid. The polyimide is then formed by means of a ring-closing reaction on this intermediate polymer. Use may be made of all the acid anhydrides and diamines that are known polyimide starting materials as the starting monomers for this intermediate polymer. Examples that may be cited of the acid anhydride include pyromellitic dianhydride, biphenyltetracarboxylic dianhydride and benzophenone tetracarboxylic dianhydride. Examples that may be cited of the diamine include 4,4'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, p-phenylenediamine and m-phenylenediamine.

The polyimide intermediate polymer may be obtained by homopolymerizing these so as to give a homopolymer, or by synthesizing a copolymer from several monomers. It is also possible to copolymerize dicarboxylic acids, diols, and derivatives of these, and use the resulting copolymers as intermediate polymers of polyamideimides, polyester amide-imides and polyester imides.

The aprotic polar solvent serves both as a dispersant for dispersing the organic onium ion-containing lamellar clay mineral and also as a solvent for dissolving the polyamic acid intermediate polymer. Examples of this aprotic polar solvent that may be used include N,N-dimethylacetamide, N-methylpyrrolidone, N,N-dimethylformamide and 1,3-dimethylimidazolinone. The aprotic polar solvent dissolves the polyimide starting monomer and the

intermediate polymer, and also has affinity with the organically-converted clay mineral. For this reason, the polyimide intermediate polymer and the organically converted clay mineral are able to mutually disperse and mix well at a molecular level within the aprotic polar solvent.

5 The production method of the present invention comprises a mixing step in which the polyimide intermediate polymer and the organically converted fine clay mineral are dissolved and dispersed within the aprotic polar solvent so as to give a slurry-like liquid mixture, and a step in which this liquid mixture is spray-dried, thereby forming a polyimide-clay mineral composite in the form of a
10 finely divided powder. This mixing step can be obtained by adding the organically converted fine clay mineral directly to the solution of the polyamic acid serving as the intermediate polymer, then stirring and dispersing, or by mixing the polyamic acid solution with a liquid slurry in which the organically converted fine clay mineral has already been dispersed. Moreover, when using
15 the lamellar clay mineral, it is preferable that this first be ground to the desired state using a mixer, mill, disintegrator, or the like, as an auxiliary means for fully carrying out dispersion.

 The polyamic acid solution can be obtained by dissolving the diamine and acid dianhydride serving as the starting monomers in an aprotic polar
20 solvent, and carrying out polycondensation in this solution. By means of this, the polyimide composite powder of the present invention can be obtained. Because the organically converted clay mineral is stably and uniformly dispersed in the smallest units (at a molecular level) within the liquid mixture, when this mixed solution is spray-dried, only the solvent is removed, making it
25 possible to isolate the clay mineral as a fine powder of the polyamic acid held in a molecularly dispersed state.

 Following conversion to a powder, the ring-closing polymerization of the polyamic acid serving as the intermediate polymer may be carried forward by heating. Ring-closing polymerization can be carried out in a non-oxidizing

environment, at a temperature of 150-400°C, and for 0.1-20 hours. The clay mineral dispersion state does not change due to the ring-closing polymerization of polyamic acid. A low degree of crystallinity without crystallization of the polyimide can be maintained.

5 The polyimide composite powder of this invention is composed of an organically converted fine clay mineral and a polyimide that covers this organically converted fine clay mineral. A single powder of this polyimide composite powder may contain a plurality of fine clay mineral particles. In this case, each of the clay mineral particles may be separated and dispersed within
10 the polyimide. What is meant here by the dispersion of the organically converted clay mineral in the polyimide is that the individual clay mineral particles do not mutually cohere, but rather are individually dispersed. The reference here to the clay mineral as a lamellar clay mineral alludes to a state where each layer of the lamellar clay mineral, or the multilayer clay mineral in
15 which there is an average of five or fewer stacked layers, is randomly present. For the sake of practical use, it is preferable that at least 50%, and preferably at least 70%, of the individual particles be in a state where they are dispersed without agglomerating and forming masses.

 The polyimide composite material powder is a finely divided powder
20 suitable for compression/sinter molding, with the powder particle size being 0.1-100 μm , and preferably 1-20 μm . When the powder particle size exceeds 100 μm , the surface area becomes small and it becomes impossible to obtain a good molded body in compression/sinter molding. On the other hand, powders having a particle size of less than 0.1 μm are too fine, as a result of which
25 handling during molding decreases, which is undesirable.

 The weight ratio of the organically converted clay mineral in this polyimide composite powder, based on a value of 100 wt% for the polyimide composite material powder as a whole, is 50-99.99 parts by weight of polyimide and 0.01-50 parts by weight of organically converted clay mineral. When the

polyimide is less than 50 parts by weight and the organically converted clay mineral is 50 parts by weight or more, the amount of lamellar clay mineral in the composite material thus obtained becomes large; this results in a loss in the excellent mechanical properties and the surface smoothness of the polyimide, which is undesirable. In cases where the organically converted clay mineral is present in an amount of less than 0.01 part by weight, the amount of clay mineral that contains organic onium ions becomes too small, as a result of which the influence upon the polyimide matrix becomes small, and so this fails to constitute a modification.

Because this polyimide composite material powder is formed by spray-drying, even with heating in the ring-closing reaction, the resin maintains an especially low crystallinity and thus has excellent molding properties. This can be confirmed by the fact that a pronounced polyimide crystal peak is not observed in the range $2\theta = 10-35^\circ$ in x-ray diffraction.

In addition to the polyimide and the clay mineral, by suitably mixing into the polyimide composite powder of the present invention, where necessary, resins other than polyimides, such as polyether ketones, polysulfones, and polyamideimides, even more desirable physical properties and characteristics can be obtained. Moreover, depending on the intended aim, pigments and dyes, reinforcing agents and fillers such as glass fibers, metal fibers, metal flakes and carbon fibers, heat stabilizers, antioxidants, ultraviolet light inhibitors, light stabilizers, lubricants, plasticizers, antistatic agents and flame retardants can also be added.

In the polyimide composite powder of the present invention, the organically converted clay mineral is dispersed within the polyimide matrix while maintaining a molecularly dispersed state. As a result, by means of compression/sinter molding, this polyimide composite material powder is able to give polyimide plastic molded articles in which the clay mineral is uniformly dispersed and which have dimensional stability. When compression/sinter

molding is carried out, for instance, the linear expansion coefficient in the vertical direction is reduced by a maximum of at least 70% in the compression molding direction, thereby making it possible to increase the dimensional stability.

5 Moreover, because a lamellar clay mineral is used as the clay mineral, and the number of layers can be made small at five or less, this clay mineral can be uniformly dispersed, making it possible to give a composite powder having a higher clay mineral addition effect.

10 Because the method for producing polyimide composites of the present invention comprises spray-drying a slurry-like liquid mixture of an aprotic polar solvent in which a polyimide intermediate polymer has been dissolved and an organically converted clay mineral has been uniformly dispersed, the organically converted clay mineral dispersion state that has formed in the liquid mixture is maintained, the solvent is rapidly removed from within the fine liquid droplets,
15 and a fine powder can be formed. Consequently, this polyimide composite powder that has formed becomes a polyimide-clay mineral composite material in which the clay mineral is uniformly dispersed, and can be used in the above-mentioned molding process.

20 This polyimide-clay mineral composite can be formed either alone or as a mixture with other compositions. Examples that may be cited of other compositions include synthetic resins such as polyimide resins and polyamide resins, inorganic fillers such as clay mineral powders, and reinforcing materials such as glass fibers, whiskers or the like.

EXAMPLES

25 The invention shall now be described more concretely by means of examples.

Application Example 1

First, 120.14 g (0.6 mol) of diaminodiphenyl ether was dissolved in

1153 g of N,N-dimethylacetamide (DMAc). Next, 130.22 g (0.597 mol) of pyromellitic anhydride was added and stirring was carried out for about one hour at room temperature. The polymerization reaction proceeded exothermically, thereby giving a 12 wt% DMAc solution of polyamic acid
5 serving as the intermediate polymer of the polyimide.

Then, 100 g of Na- montmorillonite ("Kunipia" F, manufactured by Kunimine Kogyo KK) was dispersed in 3 liters of water, after which 44.1 g of laurylamine and 24.1 g of concentrated hydrochloric acid were added, and the mixture was stirred for 60 minutes at room temperature. After washing with
10 water, this was suction-filtered using a Buchner funnel, thereby giving a composite material in a hydrous state. This hydrous composite was then freeze-dried, thereby giving an organically converted clay mineral composed of montmorillonite that contained laurylammonium ions.

Next, 30.03 g (amount of montmorillonite without the organic portion,
15 21.77 g) of the Na-montmorillonite organically converted with laurylammonium ions which was prepared above was added to 683 g of DMAc and vigorously stirred in a homogenizer for one hour, thereby giving a montmorillonite dispersion (prepared so that the ultimate clay content in the resin powder became 8 wt%).

20 The organically converted montmorillonite dispersion was added to the DMAc solution of polyamic acid obtained as described above, and the mixture was vigorously stirred for two hours at 800 rpm, thereby giving a uniform mixed slurry.

This mixed slurry stock solution was then diluted by the addition of a
25 1.5- to 2-fold amount of DMAc (based on the amount of the mixed slurry stock solution), and the viscosity of the mixed slurry solution was adjusted to about 100 cp (centipoises).

The diluted slurry was then rendered to a fine powder by means of spray-drying. The spraying conditions at this time were as follows:

Spraying device: a spray-drier for organic solvents

(DA2SW-16N, manufactured by Sakamoto Giken)

Spraying process: Two-fluid nozzle technique

Hot-air temperature: 170°C

5 Air and nozzle pressure: 4 kg/cm²

Atmosphere: dry nitrogen (oxygen concentration, 0.8%)

The particle size of the organically converted clay mineral-containing polyamic acid powder obtained under the above conditions was found from examination under an optical microscope to be 1-20 μm. When the clay mineral (montmorillonite) content within the powder was quantitatively determined by the Ash Residue Method, the same amount of clay mineral as had been charged was present.

10 Ash Residue Method: After placing 0.1 g of the clay-containing polyamic acid powder in a crucible, the organic material was completely burned off by heating for 3 hours with a gas burner, thereby leaving only the clay mineral. In this way, the amount of inorganic substance within the polyamic* acid powder was determined.

20 This powder was dried at 160°C for 15 hours in a vacuum, and the polyamic acid powder was converted into polyimide powder by a ring-closing reaction.

X-ray diffraction measurements were carried out on the clay-containing polyimide powder formed, whereupon no pronounced diffraction peaks were observed within the angle region of $2\theta = 10-35^\circ$. This indicated that a polyimide powder having a low crystallinity had been obtained.

25 Next, 10 g of this powder was compression/sinter molded using a resistance-heating vacuum pressurization hot press (FVPHP-R-10, manufactured by Fuji Denpa Kogyo).

A 10 grams powder sample was placed in a cylindrical mold having a diameter of 40 mm, and the mold was evacuated for 5 minutes at room temperature. The pressure was gradually raised to 200 atmospheres, after which heating to 400°C was carried out at 10°C/min. After maintaining this state for two hours, the pressure was released and cooling was allowed to take place. The molded piece was removed when the mold temperature had fallen to 100°C or less. When this molded piece was examined under a transmission electron microscope (TEM), the clay was found to be uniformly dispersed within the polyimide in units of one to several layers.

In order to measure the linear expansion coefficient of the molded article, a test piece measuring 5 mm long, 5 mm wide and 15 mm in width was cut out of the above-described molded piece. The thickness direction of the test piece was made to coincide with a direction perpendicular to the compression molding direction. The conditions for measuring the linear expansion coefficient were as follows.

Measuring Apparatus: Thermal stress-strain measuring unit (DT-30, manufactured by Shimadzu Corporation)

Temperature Range: Room temperature to 300°C

Temperature Rise Rate: 2°C/min

Load: 500 mg

The measured values for the linear expansion coefficient were 41 $\mu\text{m}/\text{m}/^\circ\text{C}$ (1.0) at 100°C, 42 $\mu\text{m}/\text{m}/^\circ\text{C}$ (0.95) at 150°C, 44 $\mu\text{m}/\text{m}/^\circ\text{C}$ (0.92) at 200°C, and 50 $\mu\text{m}/\text{m}/^\circ\text{C}$ (0.98) at 250°C. The values in the parentheses are relative values based on the measured value of the linear expansion coefficient for the polyimide containing no clay shown in the comparative example. Thus, a value of 0.92 indicates that the linear expansion coefficient decreased 8%.

Application Example 2

Aside from the fact that the amount of organically converted clay mineral addition in Application Example 1 was 47.54 g (the amount of

montmorillonite after removal of the organic portion being 34.14 g), the procedure for hybrid production (slurry preparation, spray-drying, compression/sinter molding) was identical (the clay content at this time became 12 wt%). The organically converted clay mineral-containing polyimide powder thus obtained was a fine (1-20 μm), low crystallinity powder that contained the same amount of clay mineral as had been charged. From TEM examination of the molded pieces, the clay mineral was confirmed to be uniformly dispersed within the polyimide at the molecular level. Measurements of the linear expansion coefficient were carried out in the same manner as in Application Example 1, and the following results were obtained: 37 $\mu\text{m}/\text{m}/^\circ\text{C}$ (0.90) at 100°C, 41 $\mu\text{m}/\text{m}/^\circ\text{C}$ (0.92) at 150°C, 46 $\mu\text{m}/\text{m}/^\circ\text{C}$ (0.96) at 200°C, and 47 $\mu\text{m}/\text{m}/^\circ\text{C}$ (0.92) at 250°C. Hence, the linear expansion coefficients decreased.

Application Example 3

Aside from the fact that the amount of addition of Na-"tetrasilic" mica (the swellable mica ME100T2, manufactured by "Cope" Chemical Co.) that was organically converted with octylammonium ions by the same method as in Application Example 1 (this mica is referred to hereinafter as 8CH2-Mic) was 26.65 g (the amount of mica after removal of the organic portion being 21.77 g), hybrid production procedure (slurry preparation, spray drying, compression/sinter molding) was carried out by exactly the same method (the clay content at this time becoming 8 wt%). The clay-containing polyimide powder thus obtained was a fine (1-20 μm), low-crystallinity powder that contained the same amount of clay as had been charged. From TEM examination of the molded pieces, the clay was confirmed to be uniformly dispersed within the polyimide at the molecular level. Measurements of the linear expansion coefficient were carried out in the same manner as in Application Example 1, , and the following results were obtained: 35 $\mu\text{m}/\text{m}/^\circ\text{C}$ (0.85) at 100°C, 39 $\mu\text{m}/\text{m}/^\circ\text{C}$ (0.89) at 150°C, 39 $\mu\text{m}/\text{m}/^\circ\text{C}$ (0.81) at 200°C, and

44 $\mu\text{m}/\text{m}/^\circ\text{C}$ (0.86) at 250°C. Hence, the linear expansion coefficients decreased.

Comparative Example

Aside from dissolving 120.14 g of diaminodiphenyl ether in 1836 g of
5 DMAc, and not including an organic clay mixing step, a polyimide powder was
obtained by similarly carrying out the hybrid production procedure in
Application Example 1. This powder was a fine (1-20 μm), low-crystallinity
powder. The linear expansion coefficient was measured, whereupon the
following results were obtained: 41 $\mu\text{m}/\text{m}/^\circ\text{C}$ at 100°C, 44 $\mu\text{m}/\text{m}/^\circ\text{C}$ at 150°C,
10 48 $\mu\text{m}/\text{m}/^\circ\text{C}$ at 200°C, and 51 $\mu\text{m}/\text{m}/^\circ\text{C}$ at 250°C.

Hence, in the application examples of the invention, the linear expansion
coefficient decreased relative to the results obtained in the comparative
examples, thus indicating that the dimensional stability of the molded articles
was excellent.

CLAIMS:

1. A polyimide composite powder comprising: an organically modified fine clay mineral; and a polyimide that covers said organically modified fine clay mineral.
- 5 2. A polyimide composite powder according to Claim 1, wherein said organically modified fine clay mineral is an organically modified lamellar clay mineral, at least 50% of which with respect to the total amount of said lamellar clay mineral has 5 layers or less.
3. A polyimide composite powder according to Claim 2, wherein
10 at least 50% of said lamellar clay mineral has a single layer with respect to the total amount of said lamellar clay mineral.
4. A polyimide intermediate polymer composite powder comprising: an organically modified fine clay mineral; and a polyimide intermediate polymer prior to the ring closing reaction that covers said
15 organically modified fine clay mineral.
5. A method of producing polyimide composite powders, comprising:
 - (a) a mixing step in which a polyimide intermediate polymer and an organically modified fine clay mineral are dissolved and
20 dispersed in an aprotic polar solvent so as to give a slurry-like liquid mixture; and
 - (b) a powder conversion step in which said slurry-like liquid mixture is spray-dried, thereby forming a polyimide-clay mineral composite in the form of a finely divided powder in which said
25 organically modified fine clay mineral is dispersed within the polyimide resin.

6. A method for producing polyimide composite powders according to Claim 5, further comprising a ring-closing imidation step in which a polyimide intermediate polymer is heated and at least partially imidized after said powder conversion step.

5 7. A method for producing polyimide composite powders according to Claim 5, wherein said aprotic polar solvent is at least one selected from the group consisting of N,N-dimethylacetamide, N-methylpyrrolidone, N,N-dimethylformamide and 1,3-dimethylimidazolinone.

8. A polyimide composite molded article produced by molding
10 the polyimide composite powder cited in any of Claims 1-3, or a mixture of the same with another composition.

9. A method for producing polyimide composite molded articles comprising the step of compressing and sintering the polyimide composite powder cited in Claim 5 or 6.

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INTERNATIONAL SEARCH REPORT

Int. Patent Application No
PCT/US 97/01270

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C04B35/634 C08K9/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K C08L C08G C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 459 472 A (KABUSHIKI KAISHA TOYODA CHUO KENKYUSHO) 4 December 1991 see claims & JP 04 033 955 A cited in the application ---	1-9
A	DATABASE WPI Section Ch, Week 8315 Derwent Publications Ltd., London, GB; Class A82, AN 83-35398K XP002029613 & JP 58 036 447 A (FUJIKURA CABLE WORKS LTD) , 3 March 1983 see abstract ---	1,8,9
A	DE 38 03 075 A (BASF AG) 17 August 1989 see claims 1,6,7 ---	1,4,5,8, 9
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/01270

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 38 10 006 A (TOYOTA CHUO KENKYUSHO KK) 6 October 1988 see claims 1,2,6 ---	1,5,8,9
A	US 4 775 586 A (BOHRN WALTER J ET AL) 4 October 1988 see claims 1,5,26,29 ---	1,5,8,9
A	DE 36 32 865 A (TOYOTA CHUO KENKYUSHO KK) 2 April 1987 see claim 1 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/01270

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0459472 A	04-12-91	JP 4033955 A DE 69111696 D DE 69111696 T US 5164460 A	05-02-92 07-09-95 25-01-96 17-11-92
DE 3803075 A	17-08-89	NONE	
DE 3810006 A	06-10-88	JP 1009202 A JP 7078089 B US 4810734 A	12-01-89 23-08-95 07-03-89
US 4775586 A	04-10-88	AU 593978 B AU 1173888 A BE 1001197 A CN 1030531 A DE 3804089 A FR 2610954 A GB 2202228 A,B JP 1224250 A LU 87133 A NL 8800400 A SE 8800507 A	22-02-90 18-08-88 16-08-89 25-01-89 25-08-88 19-08-88 21-09-88 07-09-89 14-07-88 16-09-88 18-08-88
DE 3632865 A	02-04-87	JP 62252425 A JP 8022946 B JP 62074957 A US 4739007 A	04-11-87 06-03-96 06-04-87 19-04-88